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(54) Title: POWDER COATING COMPOSITION FOR LOW TEMPERATURE CURE

(57) Abstract: This invention relates to unsaturated polyester comprising endomethylenetetrahydrophthalic acid (HIMIC) units, characterised in that the polyester comprises at least 1.1 mmol unsaturation per gram polymer, whereof at least 1 mmol originates from the HIMIC units and at least 0.01 mmol is derived from an  $\alpha,\beta$ -unsaturated acid. This invention also relates to a novel powder coating composition comprising the novel polyester resin, the process for preparing the powder coating composition, the application of the powder coating composition and substrates coated with the cured powder coating composition.

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POWDER COATING COMPOSITION FOR LOW TEMPERATURE CURE

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Field of the Invention

The present invention lies within the technical field of powder coatings, suitable for coating of substrates, especially of heat sensitive substrates.

More specifically, this invention relates to a novel unsaturated polyester resin, a novel powder coating composition comprising a unsaturated polyester resin, a process for preparing the novel unsaturated resin, a process for preparing the powder coating composition, the application of the powder coating composition and substrates coated with the cured powder coating composition.

15 Description of the prior art

Powder coatings are known for a long time, and are widely used in different applications. Usually powder coatings are applied to a substrate, subsequently melted and cured at relatively high temperatures, for example between 160 °C to 220 °C. However, not all substrates can be subjected to such high temperatures of for example 160 °C. These substrates, for example wood, paper or plastic, are called heat-sensitive substrates. There is a need for powder coating compositions suitable for use on heat-sensitive substrates, which show good flow characteristics at relatively low temperatures and which are stable during production of the powder coating composition and during storage of the powder coating composition.

25 Currently three types of coating systems are known which can reach cure at low temperatures.

The first type is based on epoxy-polyester hybrid powder coating compositions containing an increased level of catalyst for the epoxy polyester reaction. These catalysts are expensive and still the flow characteristics of the composition upon heating are not adequate to obtain good coatings. Furthermore, the presence of increased catalyst levels may result in decreased stability of the powder coating composition.

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The second type is based on UV-curable powder coating compositions. These show better flow characteristics at the required applications conditions. However, the application and cure technique is relatively expensive in relation to the conventionally used powder coatings. Furthermore UV-curable powder coating compositions show  
5 difficulties in curing when certain pigments are present in the coating or when matting is needed.

The third type is based on peroxide-polyester powder coating systems. The known types of this system show good reactivity at low temperatures, however the storage stability and the stability during the production of the powder paint do not suffice.  
10 To overcome this problem, combinations of peroxide-polyester systems with conventional TGIC cure are known. However, known systems of this type are always a compromise between good reactivity and shelf life. Either the shelf life is good but the reactivity should be improved, or the reactivity is good whilst the shelf life is to be improved

The object of the present invention is to provide a powder coating  
15 composition curable at relatively low temperatures, for example 90-150 °C, showing good flow properties at the curing temperature, without instability problems during production of the powder coating composition and during storage of the powder coating composition.

#### Short description of the invention

20 The present invention surprisingly fulfils the objective with a novel powder coating composition comprising at least:

- (a) an unsaturated polyester resin comprising endomethylene tetrahydrophthalic acid units (HIMIC) and unsaturated groups derived from an  $\alpha,\beta$ -unsaturated compound, preferably an  $\alpha,\beta$ -unsaturated acid, and;
- 25 (b) an Initiator to Induce cross-linking of the unsaturated polyester (a).

A powder coating composition according to the present invention surprisingly may be used at temperatures as low as 90 °C, whilst remaining stable during the production of the powder coating composition and during storage of the powder paint.

#### Detailed description of the invention

30 The powder coating composition according to the invention comprises an unsaturated polyester resin (a) comprising endomethylene tetrahydrophthalic acid units

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(HIMIC). Preferably the unsaturated polyester resin (a) also comprises unsaturated groups derived from an  $\alpha,\beta$ -unsaturated compound, preferably an  $\alpha,\beta$ -unsaturated acid.

Preferably, the weight per unsaturation (WPU) of polyester resin (a) is at least 250 gram per mole of unsaturation ( $-C=C-$ ), to obtain a coating composition which is stable enough. More preferably the WPU is at least 300 gram per mole unsaturation, even more preferably 325 gram per mole unsaturation and most preferably 350 gram per mole unsaturation. Preferably, the WPU is at most 3000 gram per mole unsaturation to obtain a composition being sufficiently reactive; with a high WPU the gel time increases. More preferably the WPU is at most 2000 gram per mole unsaturation, even more preferably 1000 gram per mole unsaturation and most preferably 700 gram per mole unsaturation.

The molar ratio between unsaturated groups derived from a HIMIC unit (HIMIC unsaturations) to other unsaturations derived from an  $\alpha,\beta$ -unsaturated compound, preferably from an  $\alpha,\beta$ -unsaturated acid, is generally larger than 1:1, in order to obtain good stability and formation of a good network. The ratio HIMIC unsaturations: other unsaturations is preferably at most 100:1, since this has a beneficial effect on the reactivity of the powder coating composition. Preferably the ratio HIMIC unsaturations: other unsaturations is between 50:1 and 2:1, more preferably between 20:1 and 5:1.

The number average molecular weight ( $M_n$ ) of the unsaturated polyester (a) lies preferably between 1000 and 5000, more preferably between 2000 and 4000.

The unsaturated polyester (a) may be an amorphous or a semi-crystalline polyester, preferably an amorphous polyester because this kind of polyesters is easier to process.

The glass transition temperature of the unsaturated polyester (a) may range from 35 up to and including 80 °C, preferably it ranges from 40 up to and including 60 °C. Glass transition temperature is generally measured with known DSC techniques at a temperature increase of 5 °C/min.

The acid value should generally be chosen not too high, as with high acid values it has been observed that the through-cure is less advantageous. Therefore the acid value (expressed in mg KOH/g polyester (a)) is preferably smaller than 20, in order to obtain a powder coating composition that is reactive enough at low temperatures. More preferably the acid value is lower than 15, most preferably lower than 10. The acid value preferably is higher than 1, more preferably higher than 2.

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The hydroxy value should generally be chosen not too high, as with high hydroxy values it has been observed that the through-cure is less advantageous.

Therefore the hydroxy value (expressed in mg KOH/g polyester (a)) is preferably smaller than 20, in order to obtain a powder coating composition, reactive enough at low  
5 temperatures. More preferably the hydroxy value is lower than 15, most preferably lower than 10. The hydroxy value preferably is higher than 1, more preferably higher than 2.

In a preferred embodiment of the invention, both the acid value and the hydroxy value of polyester (a) is lower than 20, preferably lower than 15 and most preferably lower than 10. The acid value and the hydroxy value of polyester (a) preferably  
10 both are higher than 1, more preferably both higher than 2.

It has surprisingly been found that the negative influence of a high acid or hydroxy value in some cases can be efficiently reduced when a metal oxide is added in a sufficient amount. The metal oxide is preferably ZnO or MgO, most preferably ZnO. The amount of the metal oxide can be easily determined in routine experimentation by the man  
15 skilled in the art. A suitable amount could be for example between 0,2 and 5 w% (based on the resin), preferably between 1 and 3 w%. When the metal oxide can be used in the desired composition, the requirements for the acid and hydroxy value are less stringent.

In order to obtain a powder coating composition showing sufficient flow properties at lower temperatures, the viscosity (measured with Emilia at 160 °C) of unsaturated polyester (a) in a powder coating composition that will be cured at  
20 temperatures in the range of 90-130 °C is preferably lower than 50 Pa.s, more preferably lower than 20 Pas and most preferably lower than 10 Pas. The preferred viscosity also depends on the temperature at which the coating will be cured. As higher viscosities (as determined at 160 °C) can be tolerated when curing takes place at higher temperatures  
25 than the indicated range.

In a preferred embodiment of the invention, the unsaturated polyester resin (a) comprises at least 1.1 mmol unsaturation per gram polymer, whereof at least 1 mmol originates from the HIMIC units and at least 0.01 mmol is derived from an  $\alpha,\beta$ -unsaturated compound, preferably an  $\alpha,\beta$ -unsaturated acid. It has been shown that if the  
30 amount of unsaturations is lower, a powder coating composition comprising unsaturated polyester resin (a) and (b) an initiator to induce cross-linking of the unsaturated polyester (a) ("initiator") is not capable of sufficient cure at very low temperatures. This preferred

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unsaturated polyester resin (a) of the powder coating composition according to the invention is not known in the prior art.

The unsaturated polyester resin (a) may be obtained in several ways. The polyester (a) is preferably obtained by preparing an unsaturated polyester (a-1) in a first step, based on at least one acid and at least one alcohol component of which at least one of the acid or alcohol is an  $\alpha,\beta$ -unsaturated compound, preferably an  $\alpha,\beta$ -unsaturated acid. This first step is followed by a second step wherein (part of) the unsaturations of the unsaturated compound is reacted with cyclopentadiene (CPD) at a temperature between about 160 °C and 220 °C thereby forming HIMIC units.

In order to obtain a polyester resin (a) comprising unsaturated groups derived from an  $\alpha,\beta$ -unsaturated compound in the polyester resin (a) one can use for example two different methods.

In a first production method for polyester (a), only part of the unsaturation derived from the  $\alpha,\beta$ -unsaturated compound is reacted with cyclopentadiene (CPD) to form HIMIC units. For example only between 70-85 %, preferably approximately 80 % CPD is used in respect to the total amount of unsaturation derived from the  $\alpha,\beta$ -unsaturated compound present in unsaturated polyester (a-1), to retain unsaturation derived from the  $\alpha,\beta$ -unsaturated compound in unsaturated polyester (a). Using this production method, preferably the hydroxy value and the acid value of unsaturated polyester (a-1) is relatively low.

In a second method of production for polyester (a), at least part of the unsaturations derived from the  $\alpha,\beta$ -unsaturated compound of the unsaturated polyester (a-1) are reacted to HIMIC units, followed by a post-reaction between the hydroxy-groups present in the unsaturated polyester (a-1) and an  $\alpha,\beta$ -unsaturated carboxylic acid derivative. This way also unsaturation derived from the  $\alpha,\beta$ -unsaturated acid can be obtained in unsaturated polyester (a). Examples of a suitable  $\alpha,\beta$ -unsaturated carboxylic acid derivative is an acid, anhydride, diester acid or monoester acid, for example fumaric acid, fumaric acid ester, diethylfumarate maleate, dimethylfumarate maleate. Using this production method, preferably the hydroxy value of unsaturated polyester (a-1) is relatively high, whilst the acid value is relatively low.

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In the second method, preferably all unsaturations derived from the  $\alpha,\beta$ -unsaturated compound of the unsaturated polyester (a-1) are reacted to HIMIC units. This can be achieved by use of an excess amount of cyclopentadiene (CPD).

WO98/46690 and WO 00/66671 describe a similar reaction process to the first production method and the second production method. However in the production process disclosed in these references an excess of CPD is present thus substantially preventing the unsaturated groups in polyester (a-1) derived from an  $\alpha,\beta$ -unsaturated acid to remain in the polyester (a), making the reaction different from the first production method. Also the second production method according to the invention differs from the production method disclosed in these references, since the subsequent reaction with an  $\alpha,\beta$ -unsaturated acid derivative to introduce unsaturated groups in the polyester is not disclosed therein. The polyester resin (a) of the present invention therefore differs from the polyester resins disclosed in WO 98/46690 and WO 00/66671 in the presence of unsaturated groups derived from an  $\alpha,\beta$ -unsaturated acid.

Furthermore, these documents disclose the use of the produced resins in a crosslinking system wherein they are cured by crosslinking the resins with a crosslinker, such as for example phenolic compounds, at relatively high temperatures, in contrast to the present invention, where the unsaturated polyester resin is suitable for use in powder coatings comprising an initiator capable of being cured at relatively low temperatures.

The unsaturated polyester (a-1) is based on a reaction between at least one acid and at least one alcohol component of which at least one of the acid or alcohol components is an  $\alpha,\beta$ -unsaturated compound, preferably an  $\alpha,\beta$ -unsaturated acid.

The  $\alpha,\beta$ -unsaturated acid used during production of the unsaturated polyester (a) can be any known  $\alpha,\beta$ -unsaturated acid and/or its anhydride. Also mixtures of different  $\alpha,\beta$ -unsaturated acids and/or their anhydrides may be used. The  $\alpha,\beta$ -unsaturated acid may be a monoacid, di-acid or tri-acid. Examples of suitable  $\alpha,\beta$ -unsaturated monoacids are acrylic acid, methacrylic acid, crotonic acid, sorbic acid and cinnamic acid. Examples of suitable  $\alpha,\beta$ -unsaturated di-acids may be maleic acid, maleic acid anhydride and fumaric acid. Examples of suitable  $\alpha,\beta$ -unsaturated tri-acids are citraconic acid, citraconic acid anhydride, itaconic acid and itaconic acid anhydride.

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Preferably the  $\alpha,\beta$ -unsaturated acid is chosen from the group consisting of fumaric acid, maleic anhydride and/or crotonic acid. More preferably fumaric acid is used. Experiments have shown that unsaturated polyester (a) based on fumaric acid show very good curing properties.

5 In addition to the  $\alpha,\beta$ -unsaturated acids other di- or polyvalent carboxylic acid or mixtures thereof may be used. Examples of suitable di- or polyvalent carboxylic acids include citraconic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid, hexahydrophthalic acid, hexachloro endomethylene tetrahydrophthalic acid, dichlorophthalic acid, isophthalic acid, terephthalic acid and/or trimellitic acid or esters thereof. Preferably terephthalic acid is used  
10 additionally, since this acid has a beneficial effect on the glass transition temperature of the polyester (a). In a preferred embodiment of the invention, the unsaturated polyester (a-1) is based on at least fumaric acid and terephthalic acid as acid units.

The additional carboxylic acid can also be used in the form of an  
15 anhydride, for example tetrahydrophthalic anhydride, endomethylene tetrahydrophthalic anhydride, hexahydrophthalic anhydride, maleic anhydride or phthalic anhydride.

Generally the unsaturated polyester (a) is based on one or more aliphatic and/or cycloaliphatic mono-di- and/or polyvalent alcohols and one or more aliphatic, cycloaliphatic and/or aromatic di- or polyvalent carboxylic acids and/or esters derived  
20 therefrom.

Examples of suitable alcohols include benzyl alcohol, ethylene glycol, propylene glycol, neopentyl glycol, butane diol, hexane diol, dimethylol cyclohexane, diethylene glycol, glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol, ethoxylated bisphenol A, for example hydrated bisphenol-A, 2,2-bis-(2-  
25 hydroxyethoxy)phenylpropane and/or propoxylated bisphenol A, for example 2,2-bis-2-hydroxypropoxy phenylpropane. Examples of suitable  $\alpha,\beta$ -unsaturated alcohols are 3-butene-1,2-diol, 2-butene-1,4-diol, allyl alcohol, cinnamyl alcohol, trimethylolpropane-monoallylether, trimethylolpropane-diallylether.

Instead of or in addition to the alcohol compound(s) one or more epoxy  
30 compounds, such as for example ethylene oxide, propylene oxide and/or allylglycidyl ether may be used. Preferably, the alcohol used for producing the unsaturated polyester is ethylene glycol, propylene glycol and/or neopentyl glycol. More preferably ethylene glycol



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or propylene glycol is used because better cure results can be obtained. Most preferred is propylene glycol because of the better powder stability of the unsaturated resin (a) produced.

If desired also monocarboxylic acids may be applied. Optionally,  
5 saturated or unsaturated monocarboxylic acids, such as synthetic and/or natural fatty acids with 2 to 36 carbon atoms or esters prepared from these carboxylic acids and polyvalent alcohols such as glycerol may also be used. The presence of a monocarboxylic acid during polyester synthesis has a beneficial effect on the crosslinking efficiency of the final powder coating composition, especially for the first mentioned production method for  
10 polyester resin (a). Preferably the monocarboxylic acid is added at the end of, or in a separate step after, the polyester forming reaction. By synthesizing the unsaturated polyester resin (a) in this way at least a part of the end-groups are blocked with an acid. The amount of end-groups that becomes blocked depends on the amount of monocarboxylic acid used. It has been found that by the addition of the monocarboxylic  
15 acid, better crosslinking is obtained.

Examples of suitable monocarboxylic acids are lauric acid, stearic acid, oleic acid, linoleic acid, benzoic acid, 4-methylbenzoic acid, phenyl-acetic acid, 2-biphenylcarboxylic acid, 2-naphthoic acid, acrylic acid and/or methacrylic acid. Preferably benzoic acid is added. It has been shown that the addition of benzoic acid can have a  
20 beneficial effect to the glass transition temperature of the unsaturated polyester (a) and the powder stability.

It has also been found possible to use a di-ester instead of the monocarboxylic acid, at the end of the polyester synthesis. Examples of di-esters are diethylfumarate and diethylmaleate. In comparison with mono-acids, di-esters are  
25 preferred because of the ease of processing.

A preferred unsaturated resin (a) has as its main components fumaric acid, terephthalic acid, propylene glycol and DCPD (dicyclopentadiene).

The preparation of the unsaturated polyester (a-1) can take place via a one-step process or via a multi-step process, both commonly known in the field of  
30 polyester synthesis.

If the unsaturated polyester (a-1) preparation takes place via a one-step process, alcohols, acids, catalysts and optionally inhibitors can be esterified to the desired

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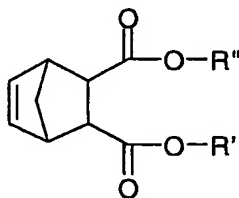
acid number or hydroxyl number at a temperature lower than 220°C. To remove low-molecular material or to obtain the desired acid number or hydroxyl number, optionally a vacuum can be applied at reduced temperature.

If the unsaturated polyester (a-1) preparation takes place in two steps, in the first step saturated acids, alcohols, catalysts and inhibitors can be esterified at temperatures between, for example, about 210°C to about 260°C during a period of about 2-10 hours, and in the second step the unsaturated compounds, acids and alcohols can be esterified at temperatures between, for example, about 180°C to about 220°C for a period of about 5-16 hours. The monomers and the reaction conditions can be varied depending on the desired properties.

If desired the usual additives may be added during the preparation of unsaturated polyester (a-1), for example catalysts, stabilizers, for example anti-colorants or polymerisation inhibitors. An example of a suitable catalyst is a Sn-based catalyst, for example FASCAT 4101 (trade mark of Atofina). An example of a suitable anti-colorant is a phosphite. An example of suitable polymerisation inhibitors are hydroquinones, phenothiazine, lithiumhydroquinone.

Following the production of the unsaturated polyester (a-1), the reaction between CPD and the unsaturations of the  $\alpha,\beta$ -unsaturated acid takes place. Preferably the following process is used in order to obtain HIMIC units.

Once the unsaturated polyester (a-1) has been obtained, dicyclopentadiene (DCPD) is added to the unsaturated polyester at temperatures between about 160 °C and about 220 °C resulting in the in-situ formation of cyclopentadiene (CPD). Next the CPD and the unsaturated groups derived from the  $\alpha,\beta$ -unsaturated acid react by a retro-Diels-Alder reaction, forming HIMIC units. This yields a group in the polyester according to formula Ia or Ib:



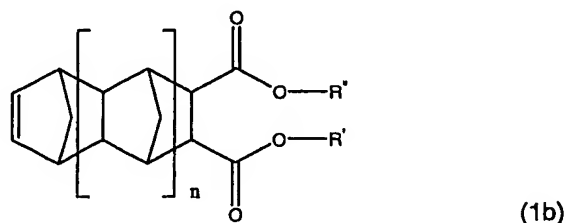
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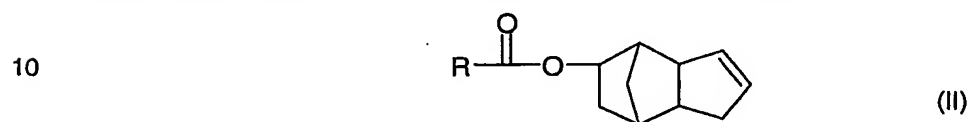
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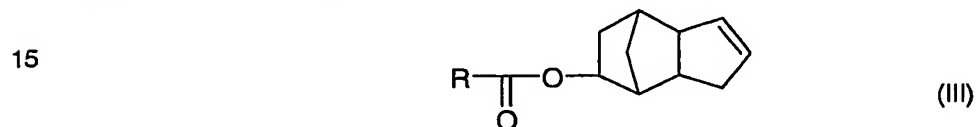


wherein R' and R'' are the same or different, part of the unsaturated polyester (a), n= 1-3.  
 5 Preferably at least 95% of the groups in the polyester are according to formula (1a) and at most 5% of the groups in the polyester are according to formula (1b).

This reaction is thus significantly different from a simple addition of DCPD to the molecule which results in the structural formula as depicted in formula II:



wherein R is a polyester, or formula III:



wherein R is a polyester.

As can be seen in formula's II and III, the resulting product in the addition  
 20 reaction of DCPD does not form HIMIC units in contrast to the process according to the invention, which yields groups according to formula Ia or Ib.

The presence of HIMIC units in the unsaturated polyester according to the invention is also crucial for obtaining the desired coating properties.

The powder coating composition according to the invention furthermore  
 25 comprises an initiator (b). The initiator is employed to generate free radicals and induce cross-linking of the unsaturated polyester resin (a) during curing of the coating upon heating. Such initiator is also called a thermal initiator. Suitable thermal initiators are

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preferably solids at room temperature. Examples of suitable thermal initiators are peroxide and azo compounds. Preferably peroxides are used.

Examples of suitable azo compounds include 2,2'-azobis(isobutyronitrile) and 2,2'-azobis(2-methylbutyronitrile).

5                   Examples of suitable peroxide initiators include peroxy ketals, diacyl peroxides, peroxy esters, dialkylperoxides, ketone peroxides. Examples of suitable peroxide initiators are cumylperoxyneodecanoate, 2,4,4-trimethylpentyl-2 peroxyneodecanoate, tert-amyl peroxyneodecanoate, bis(4-tert-butylcyclohexyl) peroxydicarbonate, bis(2-ethylhexyl) peroxydicarbonate, tert-butyl peroxyneodecanoate, 10   dibutyl peroxydicarbonate, diacetyl peroxydicarbonate, dimyristyl peroxydicarbonate, tert-amyl peroxy pivalate, tert-butyl peroxy pivalate, bis(3,5,5-trimethylhexanoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-amyl peroxy-2-ethylhexanoate, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,4-bis(tert- 15   butylperoxycarbo)cyclohexane, tert-butyl peroxyisobutanoate, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,2-bis(tert-butylperoxy)butane, tert-butylperoxy isopropyl carbonate, tert-butylperoxy 2-ethylhexyl carbonate, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, di-tert-amyl peroxide, dicumyl peroxide, bis(tert- 20   butylperoxyisopropyl)benzene, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, tert-butyl cumyl peroxide, 2,5-bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne, di-tert-butyl peroxide, diisopropylbenzene monohydroperoxide, cumyl hydroperoxide, tert-butyl hydroperoxide. Also mixtures of peroxides may be used. In this case, preferably the half-life time of the peroxides differs. This may have a beneficial effect on the curing properties of the powder 25   coating composition.

Preferably dilauroylperoxide, dibenzoylperoxyde, tert-butyl peroxy-2-ethylhexanoate, 1,4-bis(tert-butylperoxycarbo)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,2-bis(tert-butylperoxy)butane, tert-butylperoxy isopropyl carbonate, 30   tert-butylperoxy 2-ethylhexyl carbonate, tert-butyl peroxyacetate, tert-butyl peroxybenzoate is/are used.

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More preferably at least one initiator chosen from the group consisting of dilauroylperoxide, dibenzoylperoxyde, tert-butyl peroxy-2-ethylhexanoate, 1,4-bis(tert-butylperoxycarbo)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane is/are used. Most preferably dibenzoylperoxide is used,  
5 as with this peroxide a favourable balance between the half life-time and the stability is reached. Additionally dibenzoylperoxide is a solid, which facilitates easy handling.

Peroxides with a half-life time of 0.1 hour at a temperature between 75°C and 200°C are especially suitable to initiate the cure of the unsaturated polyester (a), examples of such peroxides are disclosed in for example 'Initiators for high polymers'  
10 (brochure by AKZO Nobel). Preferably initiators with a half-life time of 0.1 hour at a temperature between 90°C and 140°C are used in the powder coating composition according to the invention. Most preferably the initiator has a half-life time of 0.1 hour at a temperature between 100°C and 130°C. It has been found that the use of a catalyst for the peroxide in some cases can lower the temperature of the half-life time of the peroxides.  
15 Examples of suitable catalysts are metal salts or tertiary amines. Examples of suitable metal salts are for example based on copper or cobalt.

Preferably, the amount of initiator (b) is at most 5 wt% with respect to the unsaturated polyester (a).

Optionally a third, multiple unsaturated component (c) may be used in the  
20 composition. Surprisingly it was found that the presence of even a relatively small amount of an additional multiple, unsaturated component (c) has a desirable influence on the reactivity of the powder coating composition. Examples of suitable multiple unsaturated components are vinyl compounds or allyl compounds. Preferably the unsaturated component (c) is an allyl compound. Examples of suitable allyl compounds are  
25 triallylcyanurate (TAC), triallyltriisocyanurate (TAIC), triallyltrimelitate (TATM), 1,1,1-trishydroxymethylpropane-trimethacrylate, 1,3-diisopropenylbenzene, ethyleneglycoldimethacrylate and mixtures of any of them. Preferred co-agents are triallylcyanurate (TAC), triallyltriisocyanurate (TAIC), triallyltrimelitate (TATM), 1,1,1-trishydroxymethylpropane-trimethacrylate. Most preferred is triallyltriisocyanurate (TAIC).

30 Preferably compound (c) is present in at most 5 wt% with respect to the weight of compounds (a) and (b) together. The powder coating composition according to

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the invention can, if desired, include customary additives such as, for example, pigments, fillers, degassing agents, flow agents and stabilizers.

Suitable pigments include without limitation inorganic pigments, such as for example titanium dioxide, zinc sulphide, iron oxide and chromium oxide, as well as  
5 organic pigments, such as for example azo compounds. Suitable fillers include, for example, metal oxides, silicates, carbonates and sulphates.

Suitable stabilizers, include, for example, of primary and/or secondary antioxidants, UV stabilizers such as, for example, quinones, (sterically hindered) phenolic compounds, phosphonites, phosphites, thioethers and HALS compounds (hindered amine  
10 light stabilizers).

Surprisingly has been found that the powder coating composition according to the invention usually does not need degassing agents. If still desired for specific applications cyclohexane dimethanol bisbenzoate and the like are suitable degassing agents.

15 Suitable flow agents include for example, polyalkyl acrylates, fluorohydrocarbons and silicon oils. Other suitable additives include, for example, additives for improvement of the tribo-electric charging properties, such as sterically hindered tertiary amines, which are described in EP-B-371528.

The powder coating composition according to the invention can be  
20 prepared with any generally known process for the preparation of powder coating compositions. A more general description of how powder coating compositions can be prepared is described by Misev in Powder Coatings, Chemistry and Technology (1991, John Wiley) on pages 224-226. Care should however be taken with the temperature in used mixing equipment during the production of the powder coating composition. The  
25 temperature of the powder coating composition in the mixing equipment should be about 20 °C lower than the half-life time temperature at 0.1 hour of the used Initiator, in order to prevent early initiation of the powder coating composition. The half-life time temperature at 0.1 hour of the Initiator can be requested at the producer of the desired Initiator, or found in for example 'Initiators for high polymers' (brochure by AKZO Nobel). This enables the  
30 person skilled in the art to determine the maximal mixing temperature easily. In case several initiators are used, the temperature of the powder coating composition in the mixing equipment should be at least about 20 °C lower than the lowest half-life

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temperature at 0.1 hour of the used initiators. Suitable mixing equipment is for example an extruder or a batch mixer. Preferably an extruder is used.

Powder coating compositions according to the invention can be applied in the customary manner, for example by electrostatic spraying of the powder onto an

5 earthed substrate and curing of the coating by exposure to a suitable heating source at a suitable temperature during a sufficiently long period depending on for example the unsaturated polyester (a) and/or the substrate. The powder coating composition applied can, for example, be heated in a hot air convection oven or by means of infrared radiation (a so-called IR oven). The type of oven best to be used for a kind of substrate is well

10 known to the man skilled in the art. In general, metal substrates are cured in a convection oven and heat-sensitive substrates are cured in an IR-oven. The time the substrate is placed in an oven is called the cure time.

The preferred cure time in a hot air oven is less than 40 minutes, more preferably less than 30 minutes. Preferably the cure time in a hot air oven is at least 10

15 minutes. The preferred cure time in an IR oven is less than 20 minutes, more preferably less than 15 minutes. Preferably the cure time in an IR oven is at least 5 minutes. It was found advantageous for porous substrates to cure the powder coating composition in at least two steps: first curing is effected for a short period at a low temperature and thereafter the final cure is effected for the same or a longer period of time at a higher

20 temperature. For example first curing for 5 minutes at 100-110 °C, and thereafter curing at 120 °C. It was found advantageous for (heat) insulating substrates to apply a pre-heating step of the substrate before the curing is effected.

Compositions according to the present invention can be used in powder coatings intended for use on metal, wood, paper and plastic substrates. The powder coating

25 composition according to the invention shows exceptionally good coating properties at low cure temperatures, with respect to the conventionally available coating systems. The powder coating composition is therefore very suitable for heat sensitive substrates such as wood, paper and plastics. Examples of wood are wood, for example hardwood, hard board, wood composites, for example particle board, high, medium or low density fibre

30 board, plywood and other substrates that contain a significant amount of wood.

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The advantage of this coating composition is that it can be used at a broad temperature range, and therefore also is suitable for coating less heat-sensitive substrates, for example metals, at higher temperatures.

For heat sensitive substrates the curing temperature is preferably lower than 150 °C, more preferably lower than 140 °C, even more preferably lower than 120 °C and most preferably including and lower than 110 °C. With the powder coating composition according to the invention even good coatings can be obtained at temperatures as low as 100 °C. Preferably, the curing temperature for heat-sensitive substrates is between 100 and 120°C. Examples of combinations of cure time and curing temperature suitable for the powder coating composition according to the invention are, 5 minutes at 140°C, or 10 minutes at 130 °C, or 20 minutes at 120 °C or 30 minutes at 110 °C. The desired combination also depends on the type of oven used and the type of substrate used.

The invention also relates to the use of a coating composition according to the invention and to a substrate fully or partly coated with the cured powder coating composition according to the invention.

The invention will be further illustrated with reference to the following non-limiting examples.

Examples:

Example I: synthesis of a hydroxyl-functional fumaric resin. (Resin 1)

A 4-liter reactor with vigreux was filled with 1050.4 g terephthalic acid, 1068.5 g propylene glycol, 2 g Fascat ® 4101 (Trademark from Atofina), 1.78 g distearyl pentaerythritol diphosphite and 0.099 g lithiumhydroxyde monohydrate. The maximum resin temperature was set at 235°C and the maximum top temperature was set at 100°C. As soon as the resin became clear and the acid value (AV, in mg KOH/g resin) was below 12, the resin temperature was set at 160°C. When the resin was cooled to 160°C, 734.1 g fumaric acid, 0.198 g hydroquinone butyl ether, 0.198 g phenothiazine and 2 g Fascat 4101 were added. The maximum resin temperature was set at 198°C and the top temperature stayed at 100°C. When the top temperature dropped below 80°C, the vigreux had to be replaced by a short trap. When the new top temperature dropped below 60°C a low vacuum of 900 mbar was applied. In 1 hour the vacuum was slowly raised to 10 mbar and applied for 5 more hours.



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Properties of resin 1: AV = 6.6, hydroxyl value (OHV, in mg KOH/g resin) = 46, viscosity = 9.3 Pa.s, Tg = 46.8°C.

Example II: synthesis of a hydroxyl-functional HIMIC resin. (Resin 2)

- 5 A 1-liter reactor was filled with 400 g hydroxyl-functional resin from Example I (resin 1) and 0.06 g hydroquinone mono butyl ether. The resin temperature was set at 175°C. As soon as the resin had reached the set temperature the addition of DCPD was started. In two batches a total of 64.2 g DCPD was added. The resin was kept at 175°C for two hours. Then one hour of vacuum (10mbar) was applied. The conversion of fumaric unsaturation into HIMIC unsaturation was checked using NMR and 84% conversion was measured.
- 10 Properties of the resin 2: AV = 7.0, OHV = 34, viscosity = 6.4 Pa.s, Tg = 53.5°C.

Example III: synthesis of a hydroxyl-functional HIMIC resin with di-ester blocked end groups. (Resin 3)

- 15 A 1-liter reactor was filled with 400 g hydroxyl functional resin from Example I (resin 1) and 54.3 g diethylmaleate, 0.29 g Fascat 4101 and 0.06 g hydroquinone monobutylether. The resin temperature was set on 198°C. After 8 hours the temperature was set on 175°C. As soon as the resin had reached 175 °C the addition of the DCPD was started. In 1 batch 67.8 g DCPD was added. The resin was kept at 175°C for two hours. Then one hour of
- 20 vacuum (10mbar) was applied. The conversion of fumaric unsaturation into himic unsaturation was checked using NMR and determined to be 80%.
- Properties of the resin 3: AV = 4.3, OHV = 16, viscosity = 4.8 Pa.s, Tg = 48.3 °C.

Example IV: synthesis of a hydroxyl-functional fumaric resin with benzoic acid blocked end groups. (Resin 4)

- 25 A 4-liter reactor with vigreux was filled with 1050.4 g terephthalic acid, 1068.5 g propylene glycol, 2 g Fascat 4101, 1.78 g distearyl pentaerythritol diphosphite and 0.099 g lithiumhydroxyde monohydrate. The maximum resin temperature was set at 235°C and the maximum top temperature was set at 100°C. As soon as the resin became clear and the
- 30 AV (mg KOH/g resin) was below 12, the resin temperature was set at 160°C. When the resin was cooled to 160°C, 193.0 g benzoic acid was added. The maximum resin temperature was set at 235°C and the maximum top temperature was set at 100°C.

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As soon as the AV (mg KOH/g resin) dropped below 8, the resin temperature was set at 160°C. 734.1 g fumaric acid, 0.198 g hydroquinone butyl ether, 0.198 g phenothiazine and 2 g Fascat 4101 were added. The maximum resin temperature was set at 198°C and the top temperature stayed at 100°C.

- 5 When the top temperature dropped below 80°C, the vigreux had to be replaced by a short trap. When the new top temperature dropped below 60°C a low vacuum of 900 mbar was applied. In 1 hour the vacuum was slowly raised to 10 mbar and applied for 5 more hours. Properties of the resin 4: AV = 8.4, OHV = 14, viscosity = 4.0 Pa.s, Tg = 44.8°C.

10 Example V: synthesis of a hydroxyl-functional HIMIC resin with benzoic acid blocked end groups. (Resin 5)

A 1-liter reactor was filled with 400 g hydroxyl-functional resin with benzoic acid blocked end groups (resin 4) and 0.06 g hydroquinone mono butyl ether. The resin temperature was set at 175°C. As soon as the resin had reached the set temperature the addition of

- 15 DCPD was started. Within 1 hour 60.6 g DCPD was added. The resin was kept at 175°C for two hours. Then one hour of vacuum (10mbar) was applied. The conversion of fumaric unsaturation into himic unsaturation was checked using NMR and determined to be 86%. Properties of the resin 5: AV = 10, OHV = 5.4, viscosity = 2.1 Pa.s, Tg = 47.3°C.

20 Example VI: synthesis of a hydroxyl-functional HIMIC resin with benzoic acid blocked end groups. (Resin 6a)

A 1-liter reactor was filled with 400 g hydroxyl functional HIMIC resin (resin 2) and 28,7 g benzoic acid, 0.29 g Fascat 4101 and 0.06 g hydroquinone monobutylether. The resin temperature was set on 180°C. After 8 hours a vacuum of 400 mbar was applied. In one

- 25 hour the vacuum was slowly raised to 3 mbar. After three hours the reaction was finished. Properties of the resin 6a: AV = 10.

Example VII: synthesis of a hydroxyl-functional HIMIC resin with phenylacetic acid blocked end groups. (Resin 6b)

- 30 The synthesis of Example VI was followed, however instead of benzoic acid 32.0 g phenylacetic acid was used (resin 6b). Properties of the resin 6b: AV = 14.3.

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Example VIII: synthesis of a hydroxyl-functional HIMIC resin with 4-methyl benzoic acid blocked end groups. (Resin 6c)

The synthesis of Example VI was followed, however instead of benzoic acid 32.0 g 4-methylbenzoic acid was used (resin 6c). Properties of the resin 6c: AV = 6.5.

5

Example IX: synthesis of an acid-functional HIMIC resin. (Resin 7)

- A 1-liter reactor with vigreux was filled with 271.0 g terephthalic acid, 231.7 g propylene glycol, 0.5 g Fascat 4101, 0.45 g distearyl pentaerythritol diphosphite and 0.025 g lithiumhydroxyde monohydrate. The maximum resin temperature was set at 235°C and the maximum top temperature was set at 100°C. As soon as the resin became clear and the AV ( mg KOH/g resin) dropped below 12 the resin temperature was set at 160°C. When the resin was cooled to 160°C, 189.4 g fumaric acid, 0.02 g hydroquinone butyl ether, 0.02 g phenothiazine and 0.5 g Fascat 4101 were added. The maximum resin temperature was set at 198°C and the top temperature stayed at 100°C.
- When the top temperature dropped below 80°C, the vigreux had to be replaced by a short trap. When the new top temperature dropped below 60°C a low vacuum of 900 mbar was applied. In 1 hour the vacuum was slowly raised to 10 mbar and applied for 5 more hours. The resin temperature was set at 175°C. As soon as the resin had reached the set temperature the addition of DCPD was started. Within 1 hour 86.1 g DCPD was added.
- The resin was kept at 175°C for two hours. Then one hour of vacuum (10mbar) was applied. The conversion of fumaric unsaturation into himic unsaturation was checked using NMR and determined to be 81%. Properties of the resin 7: AV = 38.

Comparative Example A: synthesis of an acid-functional HIMIC resin with 100% conversion towards HIMIC unsaturations. (Comp. Resin 8)

- A 3-litre reactor vessel with thermometer, stirrer and distillation set-up was filled with 604.1 g propylene glycol, 820.6 g terephthalic acid, 160.8 g trimethylol propane, 0.05 wt.% dibutyltin oxide and 0.10 wt.% triphenyl phosphite. After this, with a nitrogen stream being supplied for 8 hours, the temperature was raised to 225°C while water was distilled off.
- After the temperature of the distilled-off water had dropped to 80°C, the mixture was cooled to 160°C, after which 764.9 g fumaric acid and 1.1 g t-butyl hydroquinone were

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added. The temperature was then raised to 205°C in 9 hours. At an acid value of 138 mg KOH/g resin, cooling to 185°C took place and a vacuum was applied for 30 minutes. Subsequently, the temperature was raised to 200 °C and 435.2 g dicyclopentadiene was metered in an hour. The temperature was then kept at 180°C for half an hour, after which

5 a vacuum was applied for half an hour.

Properties of resin Comp. Resin 8 (100% HIMIC conversion): AV= 81 mg KOH/g resin, OHV= 8 mg KOH/g resin, viscosity 140 dPas (Emila, 165°C), Tg 61°C (Mettler, TA3000, 5°C /min.)

10 Coating Example I:

In the following example the influence of different end groups is displayed.

40.43 g of resin 6a, 1.25 g dibenzoylperoxide (70% pure), 20.29 g Kronos® 2310 (TiO<sub>2</sub>) and 0.30 g Resiflow PV5® (polyacrylate flow agent from Worlee) were extrudated at 80°C, milled, sieved, applied on aluminum and cured in an oven for 15 minutes at 130°C.

The same procedure was followed for resin 2, 3, 6b, and 6c. The coatings were tested with the acetone double rub test giving the following results.

20 The acetone resistance is determined by rubbing to ad fro (double rub) a cotton swab soaked with acetone about the surface of a coating until the surface becomes soft or matt. A surface standing 100 double rubs is considered to possess a good acetone resistance.

Resin	ADR
2	14
3	100
6a	100
6b	30
6c	100

25 Coating Example II:

In the following example the influence of co-agents is displayed.

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200 g of resin 2, 12 g dibenzoylperoxide (50% pure), 3 g triallyltriisocyanurate (TAIC), and 1 g Resiflow PV5® (polyacrylate flow agent from Worlee) were extruded at 70°C, milled, sieved, applied on aluminum and cured for 15 minutes at 130°C.

5

The same procedure was followed replacing TAIC with the same amount of different co-agents. The coatings were tested with the acetone double rub test giving the following results:

Co-agent	ADR
-	47
Triallyltriisocyanurate (TAIC)	136
Triallylcyanurate (TAC)	47
Triallyltrimelitate (TATM)	110
1,1,1-trishydroxymethylpropane-trimethacrylaat	91
Ethyleneglycoldimethacrylate	119

10

Coating Example III:

In the following example the influence of a different ratio HIMIC/fumaric unsaturations is displayed.

15

Resin 4 was reacted with different amounts of DCPD following the procedure to prepare resin 5. This resulted in 3 different ratios HIMIC / fumaric unsaturation: 60/40, 78/22 and 95/5. These resins were cured via the following procedure on a gradient scale, and compared with resin 8:

20

200 g of resin, 8.6 g dibenzoylperoxide (70% pure), 3 g triallyltriisocyanurate (TAIC), 1.5 g and Resiflow PV5® (polyacrylate flow agent from Worlee) were extruded at 75°C, milled, sieved, applied on aluminum and cured for 10 minutes with a temperature gradient from 90-160°C.

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Himic / Fumaric ratio	100 ADR on gradient in °C
60 / 40	110-120
78 / 22	110-120
95 / 5	> 130
Comp. Resin 8	> 160

Coating Example IV:

- 5 In the following example the influence of ZnO is displayed.

150 g resin 5, 2.23 g TAIC, 1.14 g Resiflow PV5® (polyacrylate flow agent from Worlee), 4.5 g dibenzoylperoxide (75% pure) and 2.35 g zinc oxide (active) were extrudated at 70°C, milled, sieved, applied on aluminum and cured in 20 minutes at 120°C. The result in

- 10 acetone resistance and rheology (dynamic mechanical analysis, DMA) is given in comparison to a composition containing no ZnO.

Amount of ZnO	ADR	End modulus (Pa)
2.35 g	100	9*10e5
0 g	100	2*10e5

- 15 Zinc oxide in combination with polar end groups and TAIC also gave good results in white coatings as is shown below.

150 g resin, 75 g Kronos® 2310, 2.24 g TAIC, 1.15 g Resiflow PV5® (polyacrylate flow agent from Worlee), 2.25 g zinc oxide (active) and 6.5 g dibenzoylperoxide (70% pure) were extrudated at 75°C, milled, sieved, applied on MDF and cured in 5 minutes at 100°C followed by 15 minutes at 120°C by IR heating.

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Resin	ADR	Pencil hardness	Hot and cold check (ASTM D1211)
2	200	H	100 cycles
3	200	HB	100 cycles
4	200	H	< 80 cycles
5	200	HB	< 50 cycles
7	200	H-H2	100 cycles

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CLAIMS

1. Unsaturated polyester (a) comprising endomethylenetetrahydrophthalic acid (HIMIC) units, characterised in that the polyester comprises at least 1.1 mmol  
5 unsaturation per gram polymer, whereof at least 1 mmol originates from the HIMIC units and at least 0.01 mmol is derived from an  $\alpha,\beta$ -unsaturated acid.
2. Unsaturated polyester (a) according to claim 1 characterised in that at least a part of the end-groups is blocked with an acid, preferably with benzoic acid.
3. Powder coating composition comprising  
10 (a) Unsaturated polyester comprising endomethylenetetrahydrophthalic acid units (HIMIC)  
(b) Initiator to induce cross-linking of the unsaturated polyester (a).
4. Powder coating composition according to claim 3, characterised in that polyester (a) comprises unsaturated groups derived from an  $\alpha,\beta$ -unsaturated acid.
- 15 5. Powder coating composition according to claim 3, characterised in that polyester (a) is a polyester according to claim 1.
6. Powder coating composition according to any one of claims 3 to 5, characterised in that the powder coating composition comprises a third unsaturated compound (c).
- 20 7. Powder coating composition according to any one of claims 3 to 6, characterised in that the powder coating composition comprises a catalyst for the peroxide.
8. Powder coating composition according to any one of claims 3 to 7, characterised in that the powder coating composition comprises a metal oxide, preferably ZnO or MgO.
- 25 9. Process for preparing an unsaturated polyester (a), comprising the steps of first preparing an unsaturated polyester (a-1), based on at least  $\alpha,\beta$ -unsaturated acid and alcohol, followed by a second step wherein part of the unsaturations of the unsaturated acid is reacted with cyclopentadiene (CPD) at a temperature  
30 between about 160 °C and 220 °C thereby forming HIMIC units characterized in that an excess of fumaric unsaturations with respect to CPD is present in the unsaturated polyester (a-1).



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10. Process for preparing an unsaturated polyester (a), comprising the steps of first preparing an unsaturated polyester (a-1), based on at least  $\alpha,\beta$ -unsaturated acid and alcohol, followed by a second step wherein at least part of the unsaturations of the unsaturated acid is reacted with cyclopentadiene (CPD) at a temperature  
5 between about 160 °C and 220 °C thereby forming HIMIC units followed by a post-reaction between the hydroxy-groups present in the unsaturated polyester (a-1) and an  $\alpha,\beta$ -unsaturated carboxylic acid derivative.
11. Process for the preparation of a powder paint composition according to any one of claims 3 to 8, wherein the components are mixed in an extruder at a  
10 temperature about 20 °C lower than the half-life time temperature at 0.1 hour of the used initiator.
12. Process for preparing a coating by curing a powder coating composition according to any one of claims 3 to 8 applied on a substrate.
13. Process for preparing a coating according to claim 12 characterised in that at  
15 least two steps are applied: first curing is effected for a short period at a low temperature and thereafter the final cure is effected for the same or a longer period of time at a higher temperature.
14. Substrate fully or partly coated with a cured powder paint composition according to any one of claims 3 to 8.
- 20 15. Substrate according to claim 14, characterised in that the substrate is a heat-sensitive substrate
16. Use of a powder coating composition according to any one of claim 3-8.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL2004/000451

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7. C08G63/52 C08G63/54 C08G63/553 C09D167/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, INSPEC, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online!            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            NOGAMI, SUMITAKA ET AL: "Resin            compositions for low-temperature curable            powder paints"            XP002267800            retrieved from STN            Database accession no. 87:137415            abstract            &amp; JP 53 042340 B (ASAHI CHEMICAL INDUSTRY            CO., LTD., JAPAN)            10 November 1978 (1978-11-10)</p> <p style="text-align: center;">-/--</p>	<p>1,3-5,            12,14-16</p>

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the International search

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INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL2004/000451

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 337 137 B1 (MISEV TOSKO A ET AL) 8 January 2002 (2002-01-08) cited in the application column 2, lines 21-29; claims 1-4,9; examples I-IV column 3, lines 65,66 -----	1-5, 8-10,12, 14-16
X	US 3 956 228 A (NOGAMI SUMITAKA ET AL) 11 May 1976 (1976-05-11) column 5, line 1; claims 1,3; examples 1,resin,No.,3 -----	1,3-5,8

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